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# Model Analysis of Metal Partitioning In a Hazardous Waste Incineration System (Journal Version)

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16. ABSTRACT

Because the 1984 Amendments to the Solid Waste Act require that the wastes listed under the Resource Conservation and Recovery Act (RCRA) be passed through an analysis to assess the feasibility of banning from further land disposal, more incineration is expected to be used for disposing of either the banned wastes directly or the residues of various treatment processes. Incineration of hazardous wastes, municipal wastes and industrial sludges all produces some extent of trace metals. This paper provides a preliminary model concept for analyzing metal partitioning during incineration. The paper concludes that a model for predicting metal partitioning phenomenon is feasible and will save cost in conducting metal emission testing in the field.

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JOURNAL ARTICLE

# A Model Analysis of Metal Partitioning

## In a Hazardous Waste Incineration System

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***The 1984 Amendments to the Solid Waste Act require that wastes listed under the Resource Conservation and Recovery Act (RCRA) be analyzed to assess the feasibility of further banning from land disposal. Incineration is expected to be used more often for disposing of either the banned wastes directly or the residues of various treatment processes. Incineration of hazardous wastes, municipal wastes and industrial sludges produces some extent of trace metals. This paper provides a preliminary model concept for analyzing metal partitioning during incineration. The paper concludes that a model for predicting metal partitioning phenomena is feasible and could reduce costs in conducting metal emission testing in the field.***

It is well recognized that emissions from waste incinerators and coal combustion units contain trace quantities of toxic metals. These emissions are responsible for a significant fraction of the amount of such metals as antimony, arsenic, cadmium, nickel, selenium, vanadium and zinc found in the atmosphere.[1] Data from the Shirco incinerator studies[2] indicates that approximately 50 percent of the lead and 5 percent of the mercury originally present in the waste remains in the bottom ash after incineration. Billings *et al.*[3] determined that only 1 percent of the mercury present in coal used at a large pulverized coal furnace remained in the bottom ash.

Although the Environmental Protection Agency (EPA) and the private sector have been conducting incineration research since the enactment of the Resource Conservation and Recovery Act (RCRA), the emission of metals has not been adequately studied. A review of the existing literature found only limited data on metals emissions from field incinerator operation or trial burn studies. The data that are available is highly variable. For example, lead emission data from four different incinerator sites with air pollution control devices (APCDs) showed that from 8 to 23 percent of the lead in the waste was emitted.[4,5] Emissions data from small commercial boilers at six different sites showed the level of arsenic in the stack gas varies from 11.2 $\mu g/m^3$ to 665 $\mu g/m^3$ and the level of lead varies from 5390 $\mu g/m^3$ to 72,400 $\mu g/m^3$.[6] No quantitative explanation of these variations is available.

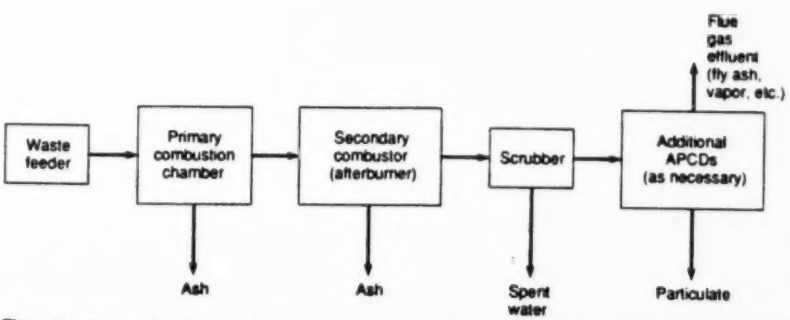


**Figure 1.** Schematic of an incineration system showing the streams into which metals may partition.

The term "partitioning" has been defined as the distribution of an element between the various materials leaving an incinerator. In addition, "partitioning" refers to the chemical and physical form of the element. Figure 1 is a simplified schematic of an incineration system showing the streams into which metals could partition. Some metals remain in the bottom ash, some vaporize and subsequently condense onto fly ash particles, and some vaporize and remain in the gas phase. The particles and vapors may be captured by scrubber water and the particles may be captured by other APCDs. The particles and vapors not captured escape into the atmosphere. The release of these particles and vapors can have a direct impact on human health. The metals which remain in the ash can be harmful to the environment because of their potential leachability.

The partitioning of metals in hazardous waste thermal destruction devices is of increasing interest to the EPA. Concern about health hazards associated with metal emissions, both to the atmosphere and by leaching into ground water from residuals, has led the EPA to consider taking regulatory actions. The need for regulation has become more pressing since the enactment of the 1984 RCRA amendments (Public Law 98-616, 1984) which ban land disposal of hazardous wastes. As a consequence of these amendments, incineration will be used more frequently to dispose of banned wastes and residues produced by treatment of banned wastes.

To establish effective regulations, the EPA must first develop a clear understanding of the processes which control metals partitioning. To aid in the development of this understanding an approach was developed which can be used to analyze some of the key phenomena which affect metals partitioning. The approach is based on develop-

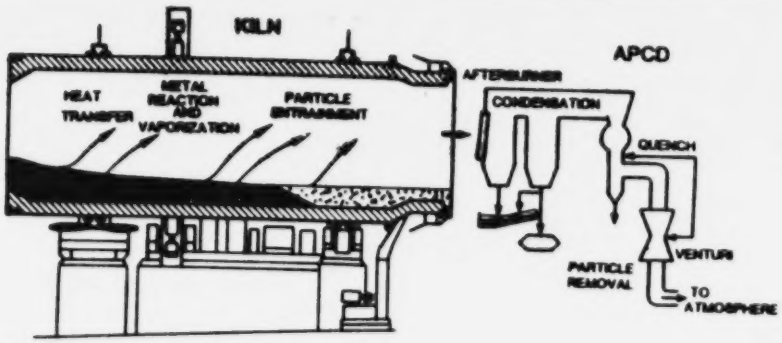


Figure 2. The phenomena controlling the partitioning of metals in a typical waste incinerator.

ment of a model to predict the behavior of metals during incineration. The model determines the behavior of metals in the combustion chamber based on the equilibrium thermodynamic state of each metal at the projected waste feed and operating conditions. This model can provide preliminary estimates of metals behavior and can be incorporated into a more comprehensive model of the partitioning of metals throughout the incinerator and APCD.[7]

### Partitioning Analysis

As shown in Figure 2, a number of phenomena play a role in determining the behavior of metals during incineration of metal bearing wastes.[8] These phenomena include:

- Vaporization of metals from the waste
- Entrainment of ash particles
- Condensation of metal vapors
- Coagulation of particulates
- Wall deposition of vapors and particulates
- Particle removal by air pollution control devices.

One of the most important of these phenomena is the vaporization of metal species from the burning waste. Most of the particles that will eventually be emitted by the incinerator are formed by the condensation of vaporized species.[9]

Metals are present in solid wastes as either small mineral inclusions in the larger organic matrix or elemental species incorporated in the structure of the organic compounds. As the organic material burns away, the metals are exposed to the hot, oxygen depleted zone immediately adjacent to the particle. As shown in Figure 3, the metal will exhibit one of the following three types of behavior:

- Vaporization
- Reaction
- No response

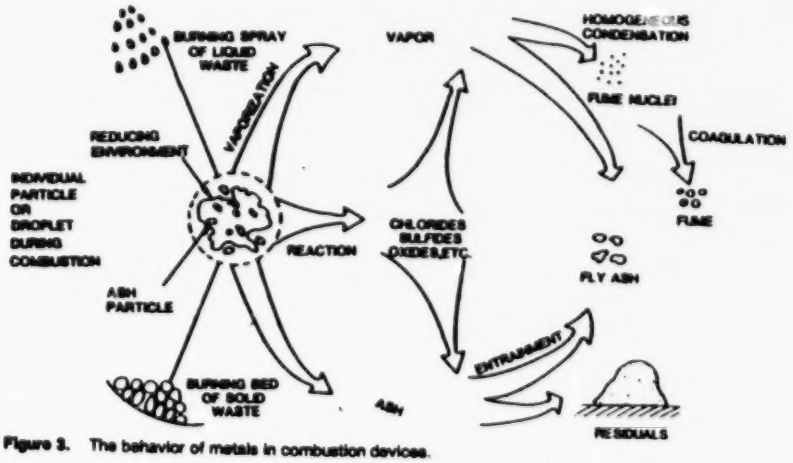


Figure 3. The behavior of metals in combustion devices.

The species which vaporize move away from the waste into a cooler, more oxygen rich atmosphere where they can undergo reactions or condense. The condensing species form new particles as well as deposit on the surfaces of particles which already exist. The newly formed particles are around 0.02 microns in diameter and grow due to coagulation and further condensation to range in size from 0.02 to 1 $\mu$m.[10]

A number of reactions can occur when metals are exposed to the atmosphere surrounding burning waste. The locally reducing conditions promote reactions in which the metals form species with lower oxidation states than are present in the original waste. In addition, the metals can react with other elements liberated from the organic matrix such as chlorine and sulfur. These newly formed species are generally more volatile than the metal species originally present in the waste.

The bulk of the metal species present in a waste will not be affected by the conditions surrounding the burning waste. These species will either remain in the bed or be entrained by the gas flow to form fly ash particles.

This paper focuses on predicting the chemical and physical form of each metal in the combustion chamber. The analysis is based on two simplifying assumptions:

1. Thermodynamic equilibrium is maintained.
2. All elements present in the waste are intimately mixed.

Although these exact conditions are rarely encountered, they approximate conditions found in wide range of practical incineration systems.

### Model Development

At equilibrium the free energy of a system is minimized. By combining this fact with mass conservation constraints it is possible to develop a series of algebraic equations which can be solved to determine the equilibrium composition of a given system.

Chemical potential is a more convenient quantity to work with than free energy. Free energy is related to chemical potential by the following equation:

$$\left(\frac{dG}{d\epsilon}\right)_{T,P} = \sum_{i=1}^{m} \nu_{ij}\mu_i$$

$$j = 1, 2, 3, \ldots, r \qquad (1)$$

where $G$ = Gibbs free energy
$\epsilon$ = extent of reaction
$T$ = temperature
$P$ = pressure

Table I. Data used in example of equilibrium program.

| Species | $i$ | $\mu_i^0$ (1100 K)[a] Kcal/mole | $N_i^0$, mole |
|---|---|---|---|
| Hg | 1 | 0.0 | 0.25 |
| $O_2$ | 2 | 0.0 | 0.50 |
| $Cl_2$ | 3 | 0.0 | 0.25 |
| HgO | 4 | 5.622 | 0.0 |
| $HgCl_2$ | 5 | −23.065 | 0.0 |

[a] JANAF Thermochemical Tables, Second Edition, 1971.

$\nu_{ij}$ = stoichiometric coefficients (reactants are negative, products positive)
$\mu_i$ = chemical potential
$m$ = number of components in the system
$r$ = number of reactions in the system

Table II. Predicted equilibrium composition of example system containing Hg, $O_2$ and $Cl_2$.

| Species | $N_i$, mole |
|---|---|
| Hg | 0.247 |
| $O_2$ | 0.500 |
| $Cl_2$ | 0.247 |
| HgO | 8.16E-14 |
| $HgCl_2$ | 0.003 |

The extent of reaction is defined by

$$N_i = N_i^0 + \sum_{j=1}^{r} \nu_{ij}\epsilon_j$$

$$i = 1, 2, 3, \ldots, m \qquad (2)$$

where $N_i^0$ = Moles of component $i$ in the initial mixture.
$N_i$ = Moles of component $i$ in the equilibrium mixture.

At thermodynamic equilibrium the free energy of a system is minimized and Equation 1 becomes

$$\sum_{i=1}^{m} \nu_{ij}\mu_i = 0$$

$$j = 1, 2, 3, \ldots, r \qquad (3)$$

Assuming that the gas behaves like an ideal gas and that the system pressure is approximately 1 atm., the chemical potential of each component can be expressed as

$$\mu_i = \mu_i^0 + RT \ln(N_i/N_T)$$
$$i = 1, 2, 3, \ldots, m \qquad (4)$$

where $\mu_i^0$ = standard state chemical potential
$R$ = universal gas constant
$N_T$ = total number of moles in the system

Equations 2, 3, and 4 comprise a system of $2m + r$ algebraic equations in $2m + r$ unknowns (the values of $N_i$, $\mu_i$, and $\epsilon_j$). It is possible to solve the system of equations and determine the equilibrium composition of a given mixture of elements at given conditions. A computer program was developed to solve this system of equations.

Table III. Ultimate composition of a typical waste.

| Element | Concentration, weight percent |
|---|---|
| C | 84.6 |
| H | 9.4 |
| Cl | 6.0 |
| Pb | 0.01 |
| Hg | 0.01 |
| Cr | 0.01 |

Table IV. List of species considered in equilibrium model analysis.

| | | |
|---|---|---|
| Hg | Pb | Cr |
| HgCl | PbCl | CrO |
| $HgCl_2$ | $PbCl_2$ | $CrO_2$ |
| HgO | $PbCl_4$ | $CrO_2Cl_2$ |
| | PbO | $CrO_3$ |
| | $PbO_2$ | $Cr_2O_3$ |
| | $Pb_3O_4$ | |

## Example Application

The purpose of this example is to illustrate how the model is used to determine the behavior of a reacting metal during incineration. A simple system consisting of three elements was used for the purposes of this illustration. The elements selected were mercury, oxygen, and chlorine. Two reactions were considered.

$$2\,Hg + O_2 = 2\,HgO \qquad (5)$$
$$Hg + Cl_2 = HgCl_2 \qquad (6)$$

Thus five chemical species are involved: Hg, $O_2$, $Cl_2$, HgO, and $HgCl_2$. These species are referred to by subscripts 1, 2, 3, 4, and 5, respectively. The reaction subscript 1 refers to Equation 5 and subscript 2 refers to Equation 6. Using Equation 3 we get

$$j = 1 \quad 2\mu_4 - 2\mu_1 - \mu_2 = 0 \qquad (7)$$
$$j = 2 \quad \mu_5 - \mu_1 - \mu_3 = 0 \qquad (8)$$

Equations for the chemical potential of each component can be obtained from Equation 4

$$i = 1 \quad \mu_1 = \mu_1^0 + RT \ln(N_1/N_T) \qquad (9)$$
$$i = 2 \quad \mu_2 = \mu_2^0 + RT \ln(N_2/N_T) \qquad (10)$$
$$i = 3 \quad \mu_3 = \mu_3^0 + RT \ln(N_3/N_T) \qquad (11)$$
$$i = 4 \quad \mu_4 = \mu_4^0 + RT \ln(N_4/N_T) \qquad (12)$$
$$i = 1 \quad \mu_5 = \mu_5^0 + RT \ln(N_5/N_T) \qquad (13)$$

From Equation 2 expressions for the mole fraction of each component in the system can be determined.

$$i = 1 \quad N_1 = N_1^0 - 2\epsilon_1 - \epsilon_2 \qquad (14)$$
$$i = 2 \quad N_2 = N_2^0 - \epsilon_1 \qquad (15)$$
$$i = 3 \quad N_3 = N_3^0 - \epsilon_2 \qquad (16)$$
$$i = 4 \quad N_4 = N_4^0 + 2\epsilon_1 \qquad (17)$$
$$i = 5 \quad N_5 = N_5^0 + \epsilon_2 \qquad (18)$$

Equations 7 to 13 are self-explanatory. The concepts represented by Equations 14 to 18 can be understood by examining Equation 14. For $i = 1$ the species is Hg. $N_1$ is the amount of Hg in the equilibrium mixture. $N_1^0$ is the amount of Hg present in the initial mixture. $2\epsilon_1$ represents the amount of Hg consumed in reaction 1 and $\epsilon_2$ represents the amount of Hg consumed in reaction 2.

There are thus twelve equations (Equations 7–18) in twelve unknowns ($\mu_1$, $\mu_2$, $\mu_3$, $\mu_4$, $\mu_5$, $N_1$, $N_2$, $N_3$, $N_4$, $N_5$, $\epsilon_1$, and $\epsilon_2$). The system of equations was solved using the data listed in Table I. The predicted equilibrium mixture at 1100 K is shown in Table II. The number of moles of each species in the equilibrium mixture ($N_i$) have been converted into mole fractions ($\chi_i$) by dividing by the total number of moles in the equilibrium mixture. These results agree with data which indicates that HgO is unstable at temperatures over 775 K.[11]

## Incinerator Analysis Using the Metals Partitioning Model

The purpose of this analysis is to demonstrate how the equilibrium based model described above can be used to examine the impact of key operating conditions on the partitioning of metals. A composition typical of simple wastes was used. This composition is shown in Table III. The waste was assumed to be a liquid with a carbon to hydrogen weight ratio of 9 to 1. The only trace metals considered were chromium, mercury and lead. The waste was assumed to contain chlorine. Thus the metals related species listed in Table IV must be considered in the equilibrium analysis. The incinerator was assumed to operate at 1100 K (1521° F) and 100 percent excess air.

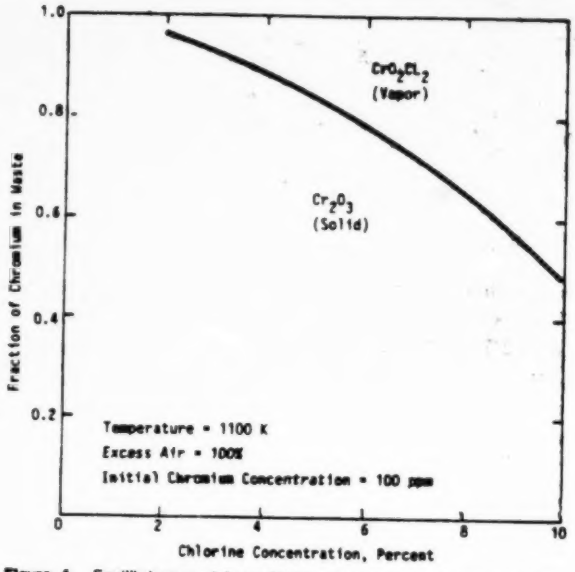


**Figure 4.** Equilibrium model prediction of the impact of waste chlorine content on the behavior of chromium.

All of the lead and mercury in the waste is predicted to vaporize under all of the conditions examined. The behavior of chromium, however, is influenced by the operating conditions.

The first parameter which was examined using the equilibrium model is the chlorine content of the waste. Figure 4 illustrates how the partitioning model predicts the chlorine concentration in the waste would affect the behavior of chromium. If the waste contains 2 percent chlorine 97 percent of the chromium would form $Cr_2O_3$ which does not vaporize at the temperatures examined and would remain with the ash. Most of the remaining 3 percent of the chromium would form $CrO_2Cl_2$. $CrO_2Cl_2$ is highly volatile and would completely vaporize at temperatures over 390 K.[11] Trace amounts of other chromium species such as $CrO_2$ and $CrO_3$ would also be formed. As the chlorine concentration increases, more of the chromium would be converted to $CrO_2Cl_2$ and vaporized. It should also be noted that the chromium in $CrO_2Cl_2$ is highly toxic hexavalent chromium while the chromium in $Cr_2O_3$ is trivalent chromium.

The second parameter that was examined is the incinerator's temperature. Temperatures from 500 K (533°F) to 1100 K (1520°F) were investigated. 1100 K is the adiabatic flame temperature for the system when 100 percent excess air is used. As shown in Figure 5, at temperatures below 700 K, over 80 percent of the chromium is predicted to form $CrO_2Cl_2$ which vaporizes at low temperatures. However as the temperature increases more $Cr_2O_3$ would be formed. At the adiabatic flame temperature, nearly 80 percent of the chromium is expected to form $Cr_2O_3$ which would *not* vaporize. This would result in more chromium in the vapor phase at 500 K than at 1100 K which is contrary to expectations. In general, as the temperature increases the quantity of metal which vaporizes increases. The quantity of $Cr_2O_3$ that vaporizes does increase with temperature and becomes significant at temperatures above 1700 K. However at the temperatures examined an insignificant amount of $Cr_2O_3$ vaporizes. This fact combined with the low concentration of chromium in the waste would be expected to cause the fraction of chromium in the vapor phase to decrease significantly as the fraction of the chromium forming $CrO_2Cl_2$ decreases.

The final parameter which was examined was the quantity of combustion air used. Figure 6 illustrates the equilibrium model's predictions of the impact of this parameter on the chromium species formed. As the amount of oxygen available increases the quantity of chromium present as hexavalent chromium in the form of $CrO_2Cl_2$ is predicted to increase. However, the impact is small compared with that of the incinerator temperature and the chlorine content of the waste.

## Conclusions

Based on the analysis in this paper it can be concluded that a theoretical model can be developed which is capa-

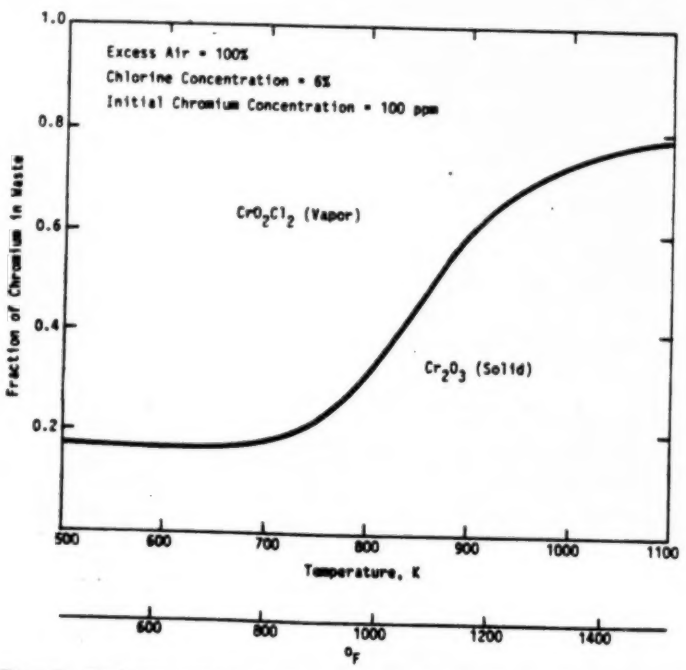


**Figure 5.** Equilibrium model prediction of the impact of temperature on the behavior of chromium.

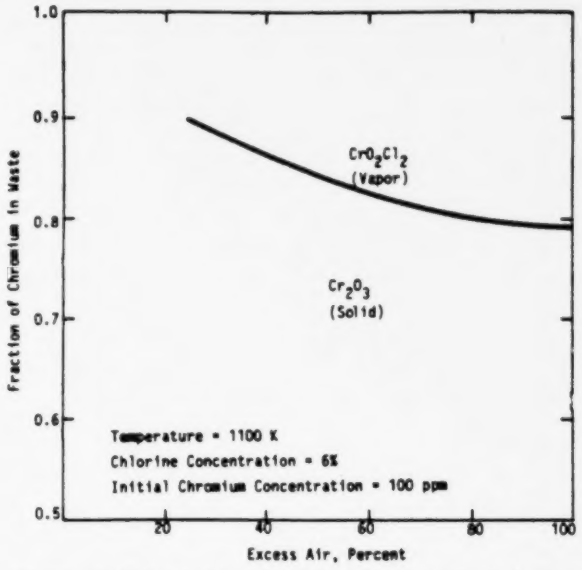


**Figure 6.** Equilibrium model prediction of the impact of combustion air on the behavior of chromium.

ble of predicting the partitioning of metals in an incinerator. Once it has been verified by field test data, the model could have a wide variety of applications. For example, permit writers could use it to estimate the accuracy and consistency of data submitted by permit applicants. Permit writers could also use the model to determine which operating parameters should be specified in a permit. The model could be used to help determine the risk associated with incinerating a metal bearing waste. It is possible to use a fully field validated model to project the fate of trace metals in an incineration system. This would be of considerable assistance in effectively designing incinerator trial burn test conditions to obtain an operating permit.


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